Active Sites for the Liquid-Phase Beckmann Rearrangement of Cyclohexanone, Acetophenone and Cyclododecanone Oximes, Catalyzed by Beta Zeolites

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The Beckmann rearrangement of oximes with different molecular sizes, i.e. cyclohexanone, cyclododecanone, and acetophenone oximes, has been studied in liquid phase at 130°C over a series of four Beta zeolites differing in the presence or absence of framework Al and internal silanol groups. When the zeolite does not contain framework Al and internal silanols, no appreciable conversion was observed. The catalyst having internal silanol groups but no framework Al exhibits oxime conversion, but the selectivity to the corresponding amide is low in some cases. In the Beta zeolite without silanol groups but containing framework Al, conversion and selectivity were found to be very high. This superior performance of Brönsted acid sites, compared to silanol groups, shows that the results reported for the vapor phase reaction cannot be extrapolated when the reaction is performed in liquid phase. Finally, as could be anticipated according to the dimensions of the micropores, it is shown that H-Beta zeolites exhibit a much better catalytic performance than H-ZSM-5 zeolite for larger sized oximes.   © 1998 Academic Press

INTRODUCTION

The Beckmann rearrangement, i.e. the transposition of ketoximes into amides, has been extensively studied for many years. The most important industrial examples are the conversion of cyclohexanone and cyclododecanone oximes into the corresponding lactams which are the precursors for the fabrication of Nylon 6 and 12, respectively. With the classical, large-scale method for synthesizing ε-caprolactam, the rearrangement of cyclohexanone oxime is carried out in the liquid phase using concentrated sulfuric acid (1). Although this procedure is very convenient from a chemical point of view, the large amount of ammonium sulfate formed during the subsequent neutralization of the oleum, the use of large amounts of fuming sulfuric acid, and the corresponding problem of corrosion make this process environmentally questionable.

In order to overcome these problems, a large number of heterogeneous catalysts, including silica (2), alumina (3), silica-alumina (4), supported boron oxide (5–7), supported tantalum oxide (8), titanium silicalites (9), zeolites (Y (10–12), Beta (13), mordenite (14), pentasil (5–7, 14–18), SAPO-11 (19), SAPO-34, and mesoporous materials (MCM-41) (20) were all tested for the vapor-phase rearrangement of cyclohexanone oxime. In this process, the reaction must be conducted at temperatures between 250 and 350°C in order to keep the oxime and products in the vapour phase. These high temperatures have a negative effect, decreasing the lactam selectivity and leading to a fast deactivation of the catalyst due to coke formation. Hence, the possibility of using a solid–liquid phase process at moderate temperatures has to be reconsidered.

A large number of works on the Beckmann rearrangement reaction using solid catalysts focuses on the nature and strength of the sites responsible for this reaction (21). Earlier papers suggested that the formation of the Brönsted amide is catalyzed by sites with medium and strong acid strengths (11, 22). However, later studies, starting with that of Sato *et al.* (14, 23), showed that both the catalytic activity and selectivity of lactam formation increase with increasing Si/Al ratio in H-ZSM-5 zeolite, leading to the use of molecular sieves with weaker acidities such as SAPO (24). More recently, it was proposed that the rearrangement of cyclohexanone oxime is not necessarily catalyzed by acidic centers but by sites with rather low or no acidity, which are sufficient to achieve high selectivity at high conversion, while maintaining the long life of the catalyst (18).

In our work, we carried out the Beckmann rearrangement of oximes of different molecular sizes in a solid–liquid reaction system. We used a series of Beta zeolites as catalysts in which the concentrations of external silanols, internal silanols, and framework Al were varied. The influence of the structure of the zeolite and the molecular size of the oxime were determined by comparing the results of experiments conducted in the presence of Beta catalysts with those using H-ZSM-5.

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TABLE 1

Nomenclature and Details of Synthesis of the Beta Samples

Sample	Gel composition	Duration of synthesis (days)
Beta-ND (Ref. (24))	SiO_2; 0.54 TEAOH; 0.54 HF; 7.25 H_2O	2.7
Beta-D	Al_2O_3; 1600 SiO_2; 864 TEAOH; 10400 H_2O; Beta-seeds[a] (3% of the total SiO_2)	18
H-Beta-ND (Ref. (25))	Al_2O_3; 50 SiO_2; 29 TEAOH; 29 HF; 362.5 H_2O	5.5
H-Beta-D (Ref. (23))	Al_2O_3; 100 SiO_2; 54 TEAOH; 1500 H_2O	16

[a] Gel composition: Al_2O_3; 50 SiO_2; 28 TEAOH; 325 H_2O; synthesis duration: 3 days (23).

EXPERIMENTAL

Catalysts

The H-ZSM-5 used was a commercial sample produced by P.Q. Industries (CBV8020). All the Beta zeolite samples were synthesized hydrothermally at 140°C, using tetraethyl-ammonium (TEA^+) as a structure-directing agent in the absence of alkali cations. The reagents used were metal Al (Meck, 99.9%), alkali-free TEAOH (35 wt% aqueous solution, Aldrich, Na < 2 ppm, K < 0.5 ppm), HF (Merck, 48%), and amorphous silica (Aerosil 200, Degussa) for the H-Beta-D sample and tetraethylorthosilicate (Merck) for the other samples. The crystallizations were carried out in PTFE-lined stainless steel 60-ml autoclaves under rotation (60 rpm). After quenching at the appropriate crystallization time, the solids were separated by centrifugation (16,000 rpm; 90 min) in the case of syntheses in OH^- media and by filtration in the case of F^- media. They were extensively washed with distilled water, dried at 100°C, and

calcined at 580°C for 3 h. The Beta-D was dealuminated with concentrated HNO_3 under reflux conditions (25) prior to calcination. The nomenclature and details of the synthesis of each sample are listed in Table 1, and some relevant properties are summarized in Table 2. The Si/Al ratio of Beta zeolites was determined by chemical analysis. Crystallinity of the samples was measured by XRD using beta-ND as the reference material. The presence of the silanol groups was established by IR (Nicolet 710 FT spectrophotometer) using self-supported wafers (∼10 mg, compressed at 2 Ton × cm^{-2}) after outgassing at 400°C under 10^{-2} Pa for 16 h. The acidity of the zeolites was determined by the standard pyridine adsorption–desorption method. Solid state ^{29}Si NMR spectra were recorded on a Varioan Unity VXR-400 WB spectrometer at 79.5 MHz, a spinning speed of SkHz, a recycle delay of 20 s and using a 55.4° pube of 4.0 μs.

Reagents

Oximes were synthezised from the corresponding ketone by reacting it with hydroxylamine hydrochloride in a mixture of ethanol and pyridine at 85°C according to the general method reported in the literature (26). The oximes were recrystallised from ethanol before use. Their identity and purity were confirmed by gas chromatography (GC) using a Hewlett-Packard 5890 instrument and a 25-m capillary column of crosslinked 5% phenylmethylsilicone and GC-MS using a Hewlett-Pakard 5988A spectrometer containing the same column type as used in the GC experiments.

Reaction Procedure

A solution of oxime (100 mg) and decane (50 mg), as the internal standard, in chlorobenzene (20 ml, Aldrich, used as received) as the solvent was heated at 130°C. The catalyst (100 mg), previously calcined at 500°C overnight, was added to the solution. The resulting suspension was

TABLE 2

Relevant Characteristics of the Zeolites Used in This Work

Sample	Si/Al	Presence of silanols	Crystal sizes[a] (μm)	Crystallinity[b] (%)	Acidity (μmol py)[c]					
					Brönsted			Lewis		
					523 K	623 K	673 K	523 K	623 K	673 K
H-ZSM-5	37	High		—	39	26	6	5	5	4
Beta-ND-1	>10000		6–8	100	d	d	d	d	d	d
Beta-ND-2	>10000		0.5–1.0	100	d	d	d	d	d	d
Beta-D	>4000	High	0.2	64	d	d	d	d	d	d
H-Beta-ND	34	Low	0.5	93	24	10	5	14	11	8
H-Beta-D	31	High	0.1	63	34	23	10	29	30	23

[a] Derived from SEM images.
[b] Of calcined samples.
[c] From extinction coef. by Emeis (32).
[d] No pyridine was detected by IR.

stirred magnetically and refluxed at the reaction temperature. The course of the reaction was followed at times ranging from 0.1 to 24 h by GC. At the end of the reaction, the catalyst was filtered and washed with CH_2Cl_2 and the organic solutions concentrated in vacuo, weighed, and analyzed by GC-MS. The zeolite was submitted to continuous solid–liquid extraction with CH_2Cl_2 using micro-Soxhlet equipment. After removing the solvent, the residue was weighed and analyzed by GC-MS. The total amount of recovered material accounted for more than 90% of the starting oxime, and no significant differences were found between the relative percentages of each compound present in the reaction liquid phase and the zeolite-extracted residue.

RESULTS AND DISCUSSION

In order to determine the activity and selectivity of silanols compared to bridging hydroxyl groups, a series of five zeolites was chosen to be used as catalysts. First, totally siliceous, highly crystalline Beta zeolites (Beta-ND) were prepared by the novel fluoride method (27, 28). The Beta-ND samples contain only external silanol groups as possible catalytic sites (see ^{29}SiMAS NMR below). A second all-silica Beta sample (Beta-D) was prepared by dealumination (25) of a zeolite with a Si/Al ratio of 800 obtained directly by synthesis using a previously described synthesis procedure (29). The lower crystallinity of Beta-D compared to Beta-ND can be quantitatively assessed by powder XRD. Figure 1 shows the corresponding diffractograms after calcination obtained exactly under the same conditions. Before calcination, Beta-ND and Beta-D were both highly crystalline. The lower crystallinity of Beta-D after the calcination step is the consequence of the presence of lattice defects and/

FIG. 2. ^{29}Si NMR of some of the catalysts used in this work.

FIG. 1. XRD patterns of calcined Beta samples.

or disruptions that introduces a significant population of internal silanol groups. As can be seen from the ^{29}Si NMR spectra shown in Fig. 2, Beta-ND (only Beta-ND-1 shown) shows a very well resolved spectrum and the absence of a peak at yields lower than −105 ppm. This indicates that the Beta-ND sample does not have structural defects, and consequently, that external silanol groups only are present in these catalysts. On the other hand, the spectrum of Beta-D is poorly resolved, and its deconvolution shows a very broad signal centered at −103 ppm, indicative of defects which are associated with internal silanol groups. Other experimental evidence for the presence of this second type of silanol group is the OH stretching region of the IR spectrum of Beta-D (Fig. 3). The external silanols are indicated by the presence of a relatively sharp band at 3745 cm^{-1}, while
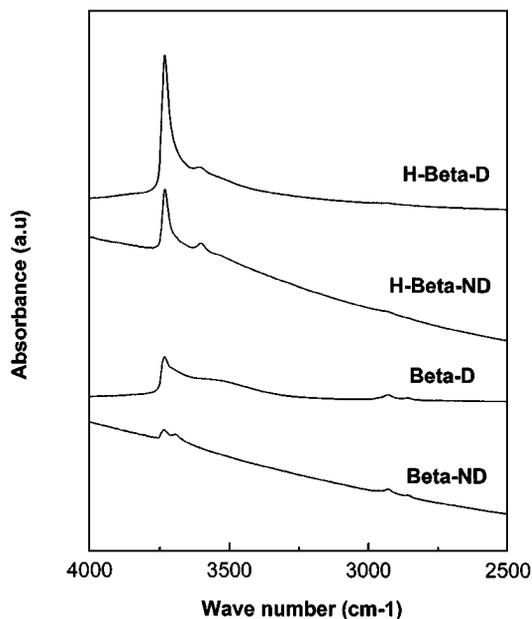
FIG. 3. IR spectrum of Beta samples.

a : R_1, $R_2 \equiv$ -(CH$_2$)$_5$-   **b :** $R_1 \equiv$ Ph ; $R_2 \equiv$ CH$_3$ **c :** R_1, $R_2 \equiv$ -(CH$_2$)$_{11}$-

the internal silanols are associated with a less well-defined broad absorption band at 3550–3700 cm^{-1}. The broadness and low frequency of this band are indicative of intense hydrogen bridge interactions in the internal silanol in contrast to the much sharper band associated with the external silanols.

From the catalytic point of view, it is anticipated that the presence of internal silanols can influence the activity of the zeolite in two different ways: (i) by having a different acid strength than the external silanols and/or (ii) by increasing the polarity of the internal voids and, thus, enhancing the absorption of the oxime inside the pores. With regard to the relative hydrophillicity/hydrophobicity of samples Beta-D and Beta-ND (point (ii)), it has been shown that, due to the remarkable hydrophobicity of Beta-ND it adsorbs 150 times more n-hexane than H$_2$O (27).

The two other Beta zeolites studied here (see Table 2) are similar to Beta-ND and Beta-D but contain Al (H-Beta-ND and H-Beta-D). Since the presence of framework Al introduces Brönsted acid sites into these solids, it should be possible to compare the activity of external silanols, internal silanols, and bridging hydroxyls $\equiv$Si(OH)Al$\equiv$.

In addition, for the sake of comparison, we also included the activity of an H-ZSM-5 zeolite sample, having a similar Si/Al ratio as the other Al-Beta zeolites (Table 2). Using these two structures, we can now discuss the influence of zeolite pore size on the reactivity of oximes of different kinetic diameters.

During the reaction (the Beckmann rearrangement) the only compounds observed, besides the starting material (**1a-c**), were the corresponding amide (**2a-c**), and the parent ketone (**3a-c**).

Other products, such as aniline or 5-cyanopent-1-ene, which were observed in other studies and arise from dehydrogenation and fragmentation, were not detected under our reaction conditions.

The results in terms of conversion, selectivity, and initial reaction rate ($\mathbf{r_0}$), measured for the liquid-phase rearrangement of cyclohexanone, acetophenone, and cyclododecanone oximes at 130°C over the different catalysts, are summarized in Tables 3 to 5. Initial reaction rates were obtained from the slope of the time-conversion plot at conversions below 10%.

It has been reported that silicalite (an all-silica pentasil structure isomorphic to ZSM-5) is the most selective catalyst for the vapor-phase Beckmann rearrangement of the cyclohexanone oxime (16). According to this, the vapor-phase results can be simply extrapolated to the liquid-phase reaction; it is expected that the best Beta zeolite catalysts will be the pure silica samples (Beta ND and Beta D). However, as can be seen in Tables 3 to 5, the three oximes are practically not transformed on the Beta-ND which have only external silanol groups, regardless of the crystallite size of the sample. The sample Beta-D, containing internal silanols, behaves differently. Beta-D gives moderate conversions, albeit the selectivity to the rearrangement was low for cyclododecanone and acetophenone oximes. Thus, we conclude that internal silanol groups have some activity in the liquid-phase transformation of oximes.

TABLE 3

Beckmann Rearrangement of the Cyclohexanone Oxime 1a

Sample	Conversion (%)	Selectivities for **2a** and/or **3a** (%)		Initial rate $\mathbf{r_0} \times 10^3$ (mol h^{-1} g^{-1})
Aerosil	5	>98	**3a**	—
H-ZSM5	67	95	**2a**	1.6
Beta-ND-1	0	—		—
Beta-ND-2	0.2	80	**3a**	—
Beta-D	38	>98	**2a**	3.1
H-Beta-ND	54	>98	**2a**	4.8
H-Beta-D	68	>98	**2a**	8.6
Amorphous SiO$_2$	0.1	72	**2a**	—

Note. Total conversion and selectivities for ε-caprolactam **2a** and cyclohexanone **3a** measured for 24 h during the reaction; initial reaction rates $\mathbf{r_0}$ are given.

TABLE 4

Beckmann Rearrangement of the Acetophenone Oxime 1b

Sample	Conversion (%)	Selectivities for 2b and/or 3b (%)		Initial rate $r_0 \times 10^3$ (mol h^{-1} g^{-1})
H-ZSM5		76	2b	
	45	24	3b	1.1
Beta-ND	0	—		—
Beta-D		92	2b	
	50	8	3b	1.4
H-Beta-ND	67	>98	2b	0.9
H-Beta-D	97	>98	2b	2.9

Note. Conversion total and selectivities for acetanilide **2b** and acetophenone **3b** measured for 24 h during the reaction; initial reaction rates **r₀** are given.

In order to discuss the potential role of the external silanol groups, which did not show any activity on the Beta-ND sample, cyclohexanone oxime was heated at 130°C in the presence of a silica (Aerosil, Degussa) with a large surface area (300 m$^2 \times$ g^{-1}) and a large population of external silanols (Fig. 2). The results of this reaction are also included in Table 3. It can be seen that, when Aerosil is used as the catalyst, the oxime conversion and the selectivity towards ε-caprolactam are much lower than that obtained with Beta-D. Furthermore, an amorphous silica (Basf, 137 m$^2 \cdot$ g^{-1}) was also used as catalyst and practically no conversion was obtained. This clearly indicates the different catalytic behaviour of the external and internal silanols of the zeolite. The external silanols are mainly responsible for the hydrolysis of the oxime to give the corresponding ketone, while the internal silanols can catalyze the Beckmann rearrangement to produce the corresponding amide. The different catalytic behavior of the two types of silanols may be related to differences in acidity, as discussed below.

When framework Al is introduced and Brönsted acidity is developed, the resulting Beta-ND is catalytically ac-

TABLE 5

Beckmann Rearrangement of the Cyclododecanone Oxime 1c

Sample	Conversion (%)	Selectivities for 2c and/or 3c (%)		Initial rate $r_0 \times 10^3$ (mol h^{-1} g^{-1})
H-ZSM5	0	—		—
Beta-ND	0	—		—
Beta-D		39	2c	
	46	38	3c	1.4
H-Beta-ND	92	>98	2c	2.8
H-Beta-D		72	2c	
	91	17	3c	5.3

Note. Conversion total and selectivities for ω-laurinlactam **2c** and cyclododecanone **3b** measured for 24 h during the reaction; initial reaction rates **r₀** are given.

tive and the selectivity for the Beckmann rearrangement is very high. This is a clear indication that bridging hydroxyl groups are active and selective for carrying out the transformation of oximes. It can be argued that the active sites are not the bridging hydroxyl groups but rather the internal silanols, generated when some of the framework Al is extracted from the framework positions during calcination. While it is true that some framework dealumination occurred during the activation of H-Beta-ND, thus creating internal silanols, the number of internal silanols formed in H-Beta-ND is much lower than that of sample Beta-D (see Fig. 2). Nevertheless, the activity of the former is higher, indicating the positive role of the Brönsted acid sites associated with framework Al. This observation is also supported by the results obtained with H-Beta-D, which gives a higher catalytic activity than Beta-D zeolite.

Thus, it appears that, while internal silanol groups are active and selective in most cases, Brönsted acid sites associated with bridging hydroxyls are even more active, exhibiting the highest selectivity for the formation of the amide. From these observations and taking into account that external silanol groups are much less active and selectively catalyze the hydrolysis to the ketone, but not the Beckmann rearrangement, we assume that the internal silanol groups are more acidic than the external silanols (30). This may be caused by the hydrogen bonding interactions of the former, as well as by the fact that the reactant is already partially activated when it penetrates the pores of the zeolite, owing to the strong electric fields on the electronic confinement occurring inside the zeolite pores (31).

If this is so, then one can conclude that nonacidic silanols preferentially catalyze the hydrolysis of the oxime, while weakly acidic and/or internal silanols can even catalyze the Beckmann rearrangement. Our results show that Brönsted hydroxyl groups, associated with framework Al, are highly active and selective sites for the formation of amides in the liquid phase. When the reaction takes place in the vapor phase, it may be the case that, at the higher reaction temperatures required, these stronger acid sites become rapidly poisoned and that most of the final observations are the result of the internal silanol groups.

Influence of the zeolite pore dimensions. It has been reported that ZSM-5 zeolite is a good catalyst for transforming cyclohexanone oxime into caprolactam under vapor phase conditions (2, 11). We confirm this fact in solution since, as can be seen in Table 3, the activity and the selectivity of ZSM-5 for **2a** are comparable to those of H-Beta-D. However, if we compare the results obtained for the transposition of acetophenone **1b** oximes (Table 4) and cyclododecanone **1c** oximes (Table 5), two ketoximes whose molecular diameter is greater than that of **1a**, then H-ZSM-5 shows a decrease in activity for the reaction with **1b** and is completely inactive when it comes to converting **1c**. Mean-

while, H-Beta-D performs the Beckmann rearrangement of **1b** and **1c** very well.

Since H-ZSM-5 and H-Beta-D have similar Brönsted acidity (see Table 2), the differences in activity are probably related to geometrical effects due to the differences in pore dimensions. Indeed, ZSM-5 zeolite has a pore size of 0.55 nm, while Beta has a pore size of 0.7 nm. Thus, the bulkier acetophenone oxime (0.7 nm) is barely able to diffuse inside the pores; an important contribution of the sites at the external surface takes place, as can be seen from the lower selectivity to the amide obtained with this reactant on H-ZSM-5. In the case of cyclododecanone oxime (0.9 nm), it is already too large to react on H-ZSM-5, and this zeolite becomes inactive. In the case of Beta, there are problems related to the diffusion of the cyclododecanone oxime, and, consequently, the contribution of the external surface to the total activity should become more important decreasing therefore the selectivity to the amide (Table 5). There is no doubt that the selectivity could be improved by silanizing the external silanol groups.

CONCLUSIONS

We have proven that external silanol groups present in zeolites may be active when the reaction is carried out at moderate temperatures in the liquid phase, and thus the oxime is hydrolyzed to give the corresponding ketone. On the other hand, internal silanols are active and selective for performing the Beckmann rearrangement (33). This may be due to a higher acidity of the internal silanols, compared to the external silanols and/or to the preactivation of the oxime in the pore of the zeolite. Under the same reaction conditions, Brönsted acid sites are very active and selective for the formation of the amide. Finally, properly prepared Beta zeolite is suitable for carrying out the Beckmann rearrangement of large size oximes, such as acetophenone and cyclododecanone oximes.

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